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Effect of Thermal Shock on Interlaminar Strength of Thermally Aged Glass Fiber Reinforced Epoxy Composites

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ABSTRACT: Glass fiber/epoxy composites were thermally conditioned at 50°C, 100°C, 150°C, 200°C and 250°C temperatures for different times and then immediately quenched directly in ice-cold water from each stage of conditioning temperature and time. The polymerization or de-polymerization by thermal conditioning and the de-bonding effect by concurrently following thermal shock in polymer composites are assessed in the present study. The short-beam shear tests were performed at room temperature on the quenched samples to evaluate the value of inter-laminar shear strength of the composites. The short conditioning time followed by thermal shock resulted in reduction of shear strength of the composites. The strength started regaining its original value with longer conditioning time. Conditioning at 250°C temperature and thereafter quenching yielded a sharp and continuous fall in the shear strength.

Key words: composites; mechanical properties; interfaces; adhesion; ageing

INTRODUCTION

Differential coefficient of thermal expansion between fiber and matrix resin in a composite may lead to residual thermal stresses at the fiber/matrix interface and is a prime cause of thermal shock. Thermal expansion coefficients in polymers are considerably high. Thus the interfacial de-bonding may occur under extremes of temperature.[1,2] Thermal shock also produces a large thermal gradient in a composite. The quenching from high temperature to low temperature generally produces tensile stresses at the surface and compressive stresses in the interior.[3] Susceptibility to de-lamination are one of the inherent weaknesses of laminated composite structures.[4] They are also susceptible to crack initiation and propagation along the laminar interfaces in various failure modes.[5] The fiber/matrix interface has always been considered as a crucial aspect of polymer composites. It is at the interface where stress concentration develops because of differences between the reinforcement and matrix phase thermal expansion coefficients. The interface may also serve as a locus of chemical reaction. The matrix of composite after curing and cooling is subject to a tri-axial stress state.[6] The mismatch of the thermal expansion coefficient between fiber and matrix is the most important reason for residual stress in polymer composite. The fiber has a lower coefficient of thermal expansion than the polymer matrix. The resulting thermal residual stresses are of compressive nature in the fiber and tensile nature in the matrix.[7] The recent study [8] showed that the thermal residual stress in glass fiber/epoxy system strongly reduces the maximum bearable load of composites.[9] The hydrostatic tensile stress severely reduces strain to failure of epoxy resin.[10,11] The objective of the present paper is to assess the inter-laminar shear strength (ILSS) of thermally conditioned glass/epoxy

laminates followed by ice-cold water quenching from the conditioning temperature. The higher conditioning temperature not only raises the degree of thermal shock but also acts like an activator [12] of the diffusion of water molecules through the composites from quenching medium. The short beam shear (SBS) test was performed here to investigate the interfacial bond strength. This characterization is valid where only the bonding level is a variable.[13]

The interactions between the fiber and matrix resin during thermal treatment are complex but important phenomena. These interactions may often lead to the formation of inter-phase. This inter-phase most probably has different composition, microstructure and properties than the bulk resin. The adhesive strength is in amorphous materials controlled by the resultant inter-atomic bonds as well as on the stresses by the reaction. The interfacial bond strength may be raised by localized chemical reactions. But it is also observed that a progressive reaction may result in the formation of a brittle reaction product. The behavior of the interfacial contact between fiber and matrix is strongly influenced by the presence and nature of residual stresses. [6]

The thermal ageing behavior of epoxy matrix composites is of particular interest because of their expanding use for structural applications in automotive and aircraft sectors where increased temperatures are very common service conditions.

EXPERIMENTAL PROCEDURES

Glass fibers of random orientation and epoxy resin (Ciba-Geigy, India LY 556), with hardener (HY 951) were used for the fabrication of laminates. The SBS

specimens from the laminated composite were exposed to 50^0C temperature. The holding times were varied (for 5, 10, 15, 20 and 25 minutes) at the conditioning temperature. The samples were quenched immediately in ice-cold water from each stage of conditioning time. The experiment was carried out at 100^0C, 150^0C, 200^0C and 250^0C temperatures. The holding times were maintained at those temperatures (like at a 50^0C temperature exposure). The SBS tests were performed on the as-quenched samples at room temperature to evaluate the value of ILSS. It is a 3-point bend test, which generally promotes failure by inter-laminar shear. The SBS test was conducted as per ASTM standard (D2344-84). The tests were carried out almost instantaneously after quenching to minimize any reversible recovery to occur in the composites.

The ILSS values were calculated as follows,

$$ILSS = 0.75p/bt$$

where p is maximum load, b the width of specimen, and t the thickness of specimen.

RESULTS AND DISCUSSION

Figure 1 shows the variation of ILSS value with the conditioning time for the as-quenched glass/epoxy composites. The specimens were conditioned first at 50^0C and 100^0C temperatures. There is a reduction in ILSS value for less conditioning time and then rise in shear values are observed with more conditioning time. The effect of thermal shock is de-bonding and it may result in fall of ILSS value. Less conditioning time yields low degree of post-curing strengthening effect. The rise in ILSS value for greater conditioning time may possibly be due to the higher order of

further polymerization. These could dominate over the de-bonding effect of thermal shock. The same trend in the variation of ILSS values is observed for the conditioning at 100^0C temperature. The fall in ILSS value at the initial level of conditioning time is more noticeable here because of greater degree of thermal shock. The higher order of thermal shock may initiate more misfit strain at the interface.

The effects of quenching on the variation of ILSS values of thermally conditioned (at 150^0C and 200^0C) temperatures for different conditioning times are shown in figure 2. The degradative effects of thermal shock are evident in both the conditioning temperatures. The reason could be the high order of thermal shock. There may also be a chance of development of greater hygrothermic stresses (fast moisture absorption by specimens from the quenching medium due to high thermal gradient) during cooling from such a high temperature. The de-bonding effect of thermal shock results in the continuous reduction of ILSS value because of the damage at the fiber/matrix interface. A slight absorption of moisture in the composite and the differences in coefficients of thermal expansion between the fiber and the epoxy resin may lead to higher residual thermal stresses at the interfaces. These could reduce the threshold stress for the interfacial de-bonding. Thus, this conditioning may initiate the nucleation for de-lamination. The rise in shear values is observed for longer conditioning times. This could be attributed to the development of stronger bond at the fiber/matrix interface due to such type of thermal exposure. Epoxy resin may be forming an interpenetrating network or further cross-linking network[2] at these conditioning temperatures and times. It is

also possible for the molecules of one surface to diffuse fast into the other that may result in greater inter-diffusion at high conditioning temperature and for longer conditioning time.[14]

The change in ILSS value of as-quenched glass fiber/epoxy laminates with conditioning time is shown in figure 3. Here the specimens were first conditioned at 250^0C temperature for different times. The continuous phenomenal fall in ILSS value with the conditioning time is reflected here. The dominating weakening effects of higher degree of thermal shock and thermal spike are observed in the test data. Epoxy resin may degrade either by chain breaks at the lower energy bond and/or by release of monomers at a chain end. Thermal degradation often leads to chain scission by de-polymerization.[15]

The fiber/matrix interfacial behavior is based on mechanical principles with the assumption made at either the level of adhesion theories or by using the surface chemistry approach.[16] The matrix shear yielding, interfacial de-bonding or a combination of both may be reflected in the SBS test. The recent studies revealed that the effect of thermal shock on interfacial damage of thermally and cryogenically conditioned Kevlar/epoxy and Kevlar/polyester composites is not very conclusive.[17,18] The probable reasons for the inconceivable and inconsistent behavior of polymeric composites could be attributed to the post-curing hardening effects of thermal conditioning, the development of compressive stresses by quenching and also the de-bonding effect of thermal shock. The resultant residual stresses are the manifestation of those phenomena.

An interfacial reaction may impart different morphological modification to the matrix resin microstructure in proximity to the fiber surface. The interactions between fiber and polymer matrix during thermal treatment are important phenomena. The existence of a weak boundary layer in glass/epoxy composites may be interpreted by the migration of curing agent to the interface. The layer has a lower molecular mobility compared to the bulk resin.[19-21] The micro-structural gradient may promote crack initiation and propagation through this layer.[22-24] The properties of this layer are believed to be more brittle than the bulk matrix having stoichiometric ratio between epoxy and curing agent.[25]

Environmental exposure results in reduced interfacial stress transmissibility because of matrix polymer plasticization, chemical degradation and mechanical damage.[26-28] Matrix plasticization reduces matrix modulus. Chemical degradation is the result of weakening of the bonds at the fiber/matrix interface. Mechanical degradation here is a function of thermal shock misfit strain at the interface. The strain pulls the epoxy away from the fiber.

A significant chemical and structural change usually may take place during thermal ageing. These changes in epoxy matrix can exert an influence on mechanical properties of a fiber reinforced composite.[29] The adhesive bond strength represent the cumulative effect of multiple weak bonds acting in concert. The successive opening of intra-chain loops or folded domains under stress in a cross-linked multi-chain matrix avoids the breaking of strong bond until all domains are unfolded or opened.[30] High temperature thermal ageing and subsequent hydrothermal ageing with a temperature gradient may promote irreversible effects of the epoxy resin,

especially in the vicinity of the substrate.[31] All these factors may modify the local stress threshold required for breaking of strong bond of adhesion at the fiber/polymer interface. That eventually could initiate additional matrix cracking[21] and also other damages in the interfacial region of a composite. Micro- and macro-damages are evident in the scanning electron micrograph of the treated specimen in Figure 4. A SEM micrograph with the same magnification of fractured surface for untreated composites is shown in Fig. 5. It possibly reveals a large area of resin matrix with comparatively very less matrix and interfacial damages.

CONCLUSION

It may be reasonable to state that at low thermal conditioning temperature, the de-bonding effect of thermal shock is not noticeable except for the less conditioning time. There is a possibility of an improvement in ILSS value because of dominating post-curing phenomena. The higher conditioning temperature is adversely affecting the interfacial properties due to the higher degree of thermal shock. The very strong weakening effect of thermal degradation and thermal shock is evident in glass/epoxy composites for the conditioning at 250^0C temperature and thereafter, following thermal shock treatment. Many factors are contributing for the nature of interfacial behavior of composite materials in such active and complex environment.

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Figure Captions

Figure 1 Effect of thermal shock on ILSS of thermally conditioned (at 50°C temperature [●] and at 100°C temperature [♦]) glass/epoxy composites.

Figure 2 Effect of thermal shock on ILSS of thermally conditioned (at 150°C temperature [●] and 200°C temperature [♦]) glass/epoxy composites.

Figure 3 Effect of thermal shock on ILSS of thermally conditioned (at 250°C temperature) glass/epoxy composites.

Figure 4 Scanning electron micrograph shows matrix and de-bonded areas of the treated samples at a 750 magnification.

Figure 5 Scanning electron micrograph of the untreated specimens at a 750 magnification.

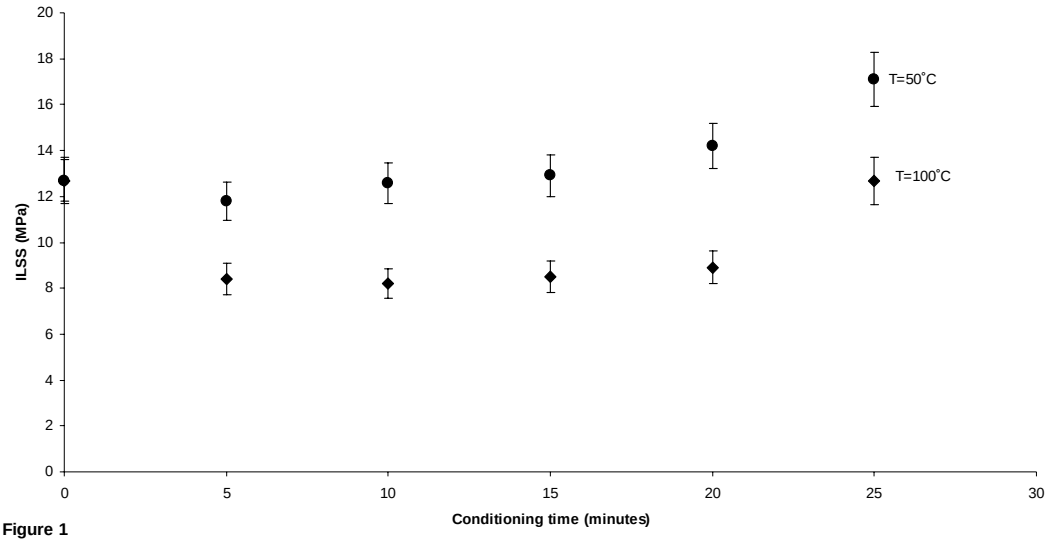
ILSS (MPa)
Conditioning time (minutes)
T=50˚C
T=100˚C
0
2
4
6
8
10
12
14
16
18
20
0
5
10
15
20
25
30

Figure 1

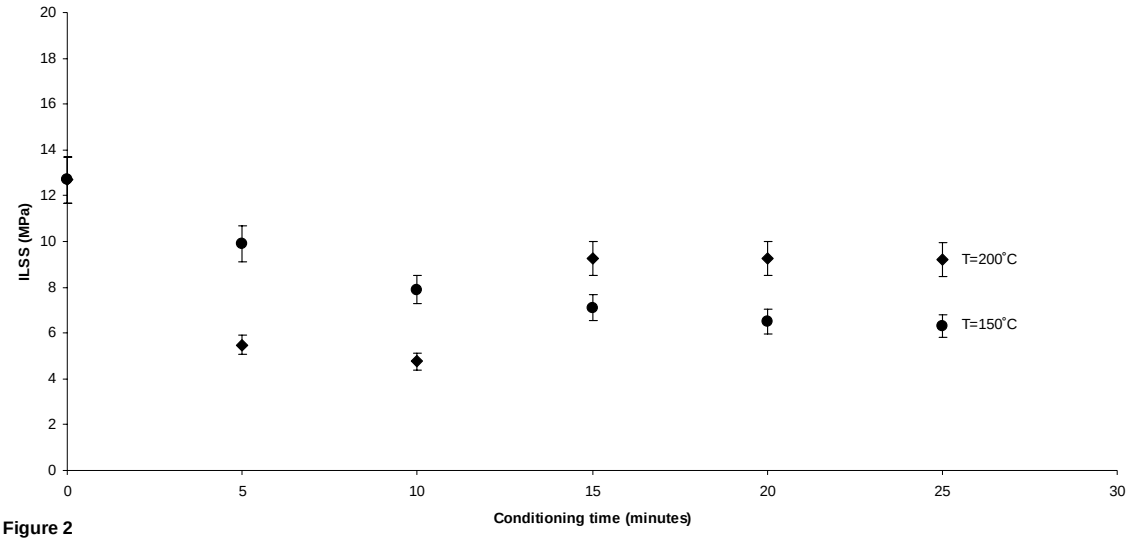
ILSS (MPa)
Conditioning time (minutes)
T=200˚C
T=150˚C
0
2
4
6
8
10
12
14
16
18
20
0
5
10
15
20
25
30

Figure 2

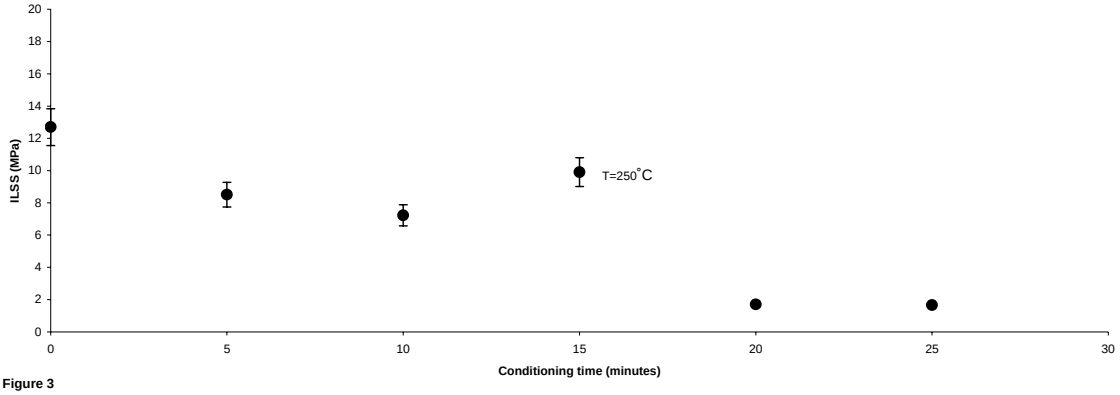
ILSS (MPa)
Conditioning time (minutes)
T=250°C
0
2
4
6
8
10
12
14
16
18
20
0
5
10
15
20
25
30

Figure 3

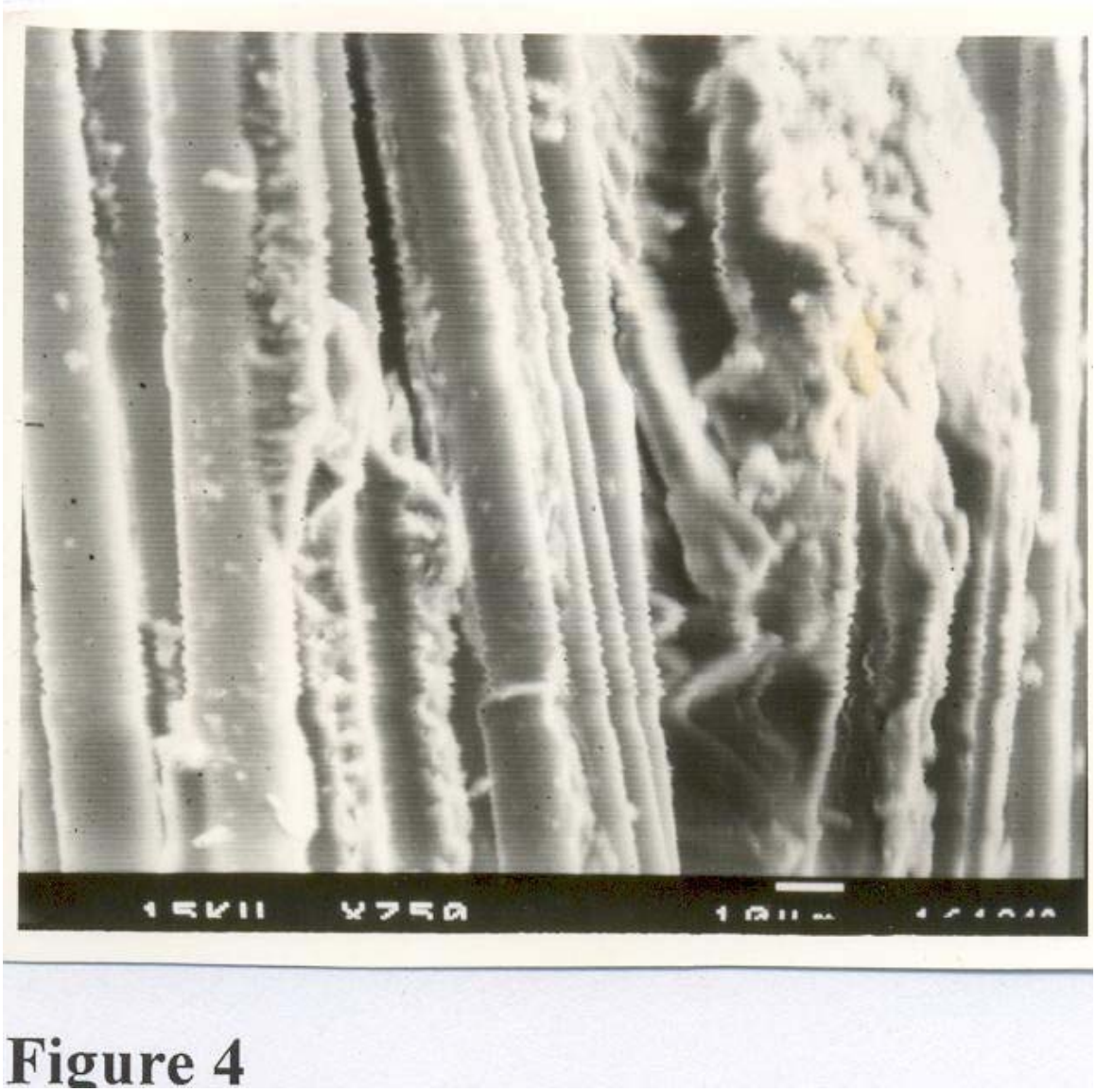

Figure 4

Figure 4

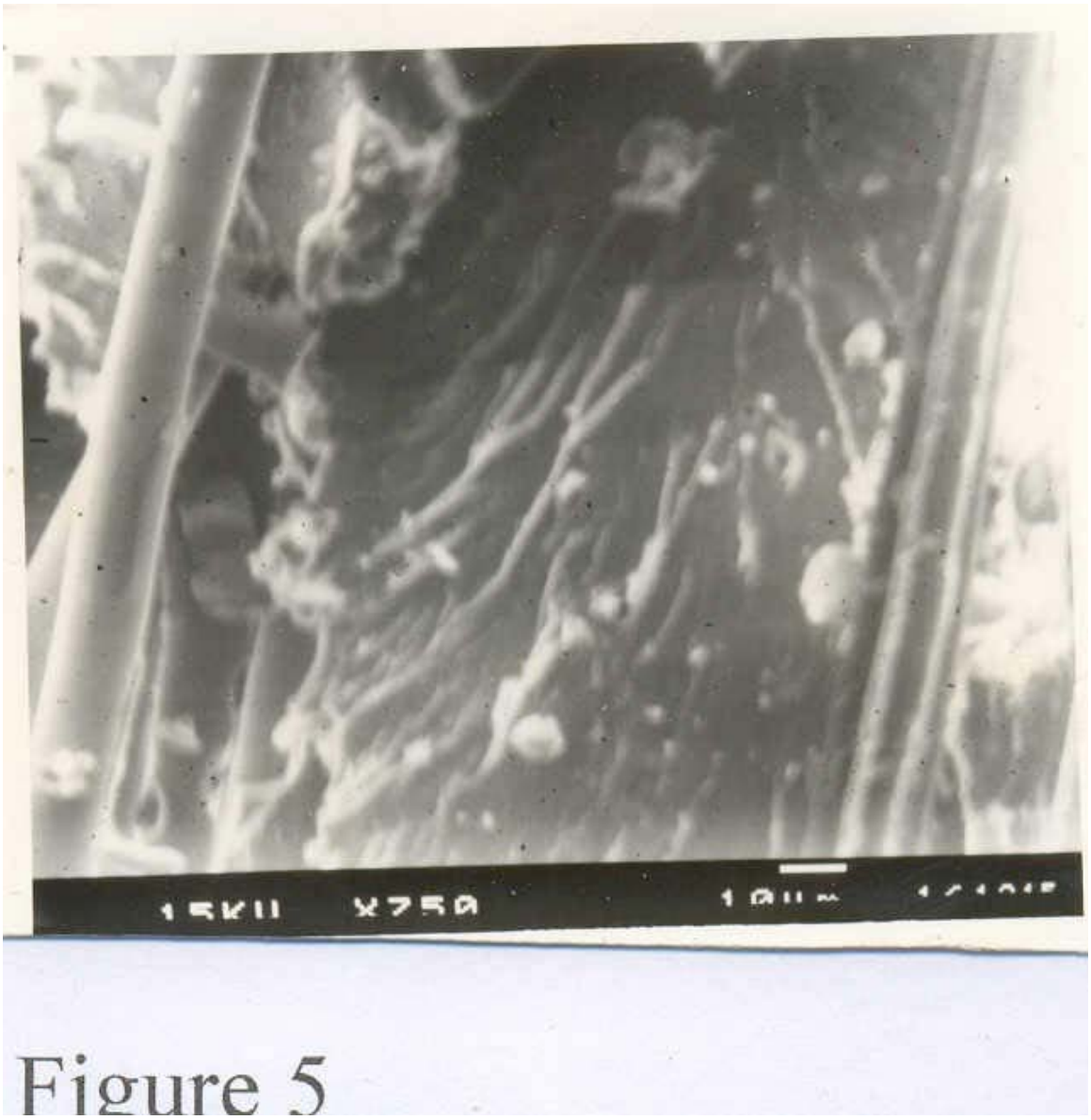

Figure 5